

Electrocatalytic Reduction of Carbon Dioxide to Methane on Single Transition Metal Atoms Supported on a Defective Boron Nitride Monolayer: First Principle Study

Xin Tan,* Hassan A. Tahini, Hamidreza Arandiyani, and Sean C. Smith*

The electrochemical conversion of carbon dioxide (CO₂) and water into useful multi-electron transfer products, such as methanol (CH₃OH) and methane (CH₄), is a major challenge in facilitating a closed carbon cycle. Here, a systematic first principle study of the potential of single transition metal atoms (Sc to Zn, Mo, Rh, Ru, Pd, Ag, Pt, and Au) supported on experimentally available defective boron nitride monolayers with a boron monovacancy (TM/defective BN) to achieve highly efficient electrocatalytic CO₂ reduction (ECR) to CH₄ is carried out. Our computations reveal that Fe/defective BN, Co/defective BN, and Pt/defective BN nanosheets possess outstanding ECR activities with quite low (less negative) onset potentials of −0.52, −0.68, and −0.60 V, respectively. Given that Fe and Co are nonprecious metals, Fe/defective BN and Co/defective BN may provide cost-effective electrocatalysts. The high ECR activities of these TM/defective BN catalyst systems stem from the moderate electrocatalysts' affinities for C and O, which modulate the free energies of ECR intermediates in the reaction pathways. Moreover, it is found that Fe/defective BN and Pt/defective BN show high selectivity of ECR to CH₄. This finding highlights a strategy to design highly active and selective single-atom electrocatalysts for ECR to CH₄.

Electrocatalytic CO₂ reduction (ECR) to chemical fuels or other useful chemicals, using only water, CO₂, and electricity as inputs, has attracted considerable attention as a promising process because of its straightforward operation in comparison to high-temperature reactors.^[4–10] According to the number of transferred electrons and protons in the ECR, a wide variety of product channels is in principle accessible, including the two-electron products carbon monoxide (CO), formaldehyde (HCHO), and formic acid (HCOOH); the six-electron product methanol (CH₃OH); and the complete eight-electron product methane (CH₄);^[11–14] not to mention the competitive hydrogen evolution reaction (HER). This promising technique is hampered by the lack of efficient ECR electrocatalysts that are capable of reducing CO₂ beyond the two-electron products, such as CH₃OH and CH₄, with CH₄ being one of the simplest hydrocarbons and a primary component of natural gas with an existing infrastructure for storage, distribution, and consumption.^[15–18]

1. Introduction

Utilization of carbon dioxide (CO₂) as a carbon source to synthesize valuable chemicals has the potential to mitigate the greenhouse effect while generate high-energy density fuels and other commodities.^[1,2] Due to CO₂'s inherent thermodynamic stability and chemical inertness, the activation of CO₂ and its subsequent hydrogenation to hydrocarbons is challenging.^[3]

Although many heterogeneous and homogeneous electrocatalysts have been screened for their effectiveness in the ECR to multi-electron transfer products in both experiments and computations for many decades, the availability of efficient electrocatalysts is still very limited. Pure metallic Cu is the only transition metal (TM) that selectively promotes ECR to hydrocarbons, predominantly CH₄, with significant quantities (faradaic efficiency $\approx 72.3\%$) at high current densities ($\approx 5 \text{ mA cm}^{-2}$).^[19–23] However, the ECR on Cu requires a prohibitively high overpotential (on the order of 1 V), making Cu an inefficient electrocatalyst for the ECR. Well-dispersed Cu nanoparticles supported on glassy carbon have been successfully prepared, which show enhanced electrochemical methanation of CO₂ comparable to those of much more expensive Cu single-crystal electrodes.^[15] Both experimental and theoretical analysis have suggested that Mo₂C electrocatalysts are capable of ECR into CH₄ fuel at low onset potential ($\approx -0.55 \text{ V}$), while an acceleration of the competitive HER was also observed in the presence of CO₂.^[24,25] In addition, Li et al. has predicted from density functional theory (DFT) calculations that the Cr₃C₂ and Mo₃C₂ MXenes exhibit promising CO₂ to CH₄ selective conversion capabilities.^[26]

Dr. X. Tan, Dr. H. A. Tahini, Prof. S. C. Smith
Integrated Materials Design Laboratory
Department of Applied Mathematics
Research School of Physics and Engineering
The Australian National University
Canberra, ACT 2601, Australia
E-mail: Xin.Tan@anu.edu.au; Sean.Smith@anu.edu.au
Dr. H. Arandiyani
Laboratory of Advanced Catalysis for Sustainability
School of Chemistry
The University of Sydney
Sydney, NSW 2006, Australia

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Recent DFT and experimental results have shown that the use of graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) as a molecular scaffold to coordinate the active Cu centers (Cu- C_3N_4 complex) presents a new molecular-level strategy for the development of electrocatalysts with high ECR selectivity toward hydrocarbon/alcohol.^[27] Clearly, both theoretical and experimental investigations are proving important to develop high-performance electrocatalysts for the ECR to multi-electron transfer products.

Single-atom catalysts (SACs), in which single metal atoms anchored to supports, have recently emerged as a new research frontier in the catalysis community.^[28–33] With uniform single-atom dispersion and well-defined configuration, SACs not only represent the cost-effective utilization of precious metallic catalysts, but also open up considerable new territory for optimizing selectivity and activity for various reactions. Very recently, DFT calculations have been performed to systematically study the possibility of a series of single TM atoms supported on the experimentally available defective boron nitride monolayer with a boron monovacancy (TM/defective BN) as nitrogen fixation electrocatalysts.^[34] The results revealed that Mo/defective BN nanosheets are very stable and possess outstanding nitrogen fixation electrocatalytic activity, which opens a new avenue of ammonia production by SACs under ambient conditions.

In this work, we use first principle DFT computations to systematically investigate the potential of TM/defective BN (TM = Sc to Zn, Mo, Rh, Ru, Pd, Ag, Pt, and Au) as highly efficient electrocatalysts for ECR to CH_4 . Our DFT results demonstrate that Fe/defective BN, Co/defective BN, and Pt/defective BN possess outstanding ECR activities with quite low (less negative) onset potentials of -0.52 , -0.68 , and -0.60 V, respectively, which are less negative than other ECR electrocatalysts, such as Cu (100) (-0.78 V), Cu (211), (-0.67 V), and Cu- C_3N_4 complex (-0.75 V). Given that Fe and Co are nonprecious metals, Fe/defective BN and Co/defective BN are cost-effective electrocatalysts. The high ECR activities of those TM/defective BN stem from moderate electrocatalysts' affinities for C and O, which modulate the free energies of ECR intermediates in the reaction pathways. Moreover, we also find that Fe/defective BN and Pt/defective BN show high selectivity of ECR to CH_4 . These findings clarify the ECR mechanism on TM/defective BN and offer a strategy to design highly active and selective single-atom electrocatalysts for ECR to CH_4 .

2. Results and Discussion

2.1. CO_2 Adsorption on Various TM/defective BN Nanosheets

Given that chemisorption of CO_2 on electrocatalysts is the first step that occurs during the ECR, which guarantee sufficient activation of the inert CO_2 molecule, we first study the CO_2 adsorption on a series of 3d, 4d, and 5d TM atoms (TM = Sc ~ Zn, Mo, Rh, Ru, Pd, Ag, Pt, and Au) supported by a defective BN nanosheet. Here, we consider two CO_2 adsorption configurations: the CO_2 may interact with TM/defective BN either through physisorption, where CO_2 is attached to the surface through a noncovalent interaction between the O atom of CO_2 and the TM atom (Figure 5b), or through chemisorption, in which the C atom of CO_2 is formally bound with the TM atom

(Figure 5c). To determine the thermodynamic stability of CO_2 on TM/defective BN, we calculate the adsorption energy (E_{ads}) of CO_2 , which defined as $E_{\text{ads}} = E_{\text{CO}_2+\text{TM}/\text{BN}} - E_{\text{TM}/\text{BN}} - E_{\text{CO}_2}$, where $E_{\text{CO}_2+\text{TM}/\text{BN}}$, $E_{\text{TM}/\text{BN}}$, and E_{CO_2} represent the total energy of the TM/defective BN with adsorbed CO_2 , the bare TM/defective BN, and the isolated CO_2 molecule, respectively. Figure 5d shows the E_{ads} of CO_2 on various TM/defective BN. On Sc, Ni, Cu, Zn, Pd, Ag, and Au atoms supported by a defective BN, CO_2 is only physisorbed on the electrocatalysts, suggesting that those nanosheets are inappropriate as ECR electrocatalysts due to their poor performance for CO_2 activation. On the other hand, CO_2 is both physisorbed and chemisorbed on other 10 atoms (including Ti ~ Co, Mo, Ru, Rh, and Pt) supported by a defective BN. Furthermore, those nanosheets seem to be active toward CO_2 chemisorption, exhibiting spontaneous adsorption energies between -1.25 and -0.14 eV. Those TM/defective BN nanosheets that are seen to facilitate the chemisorption of CO_2 molecule are potential electrocatalysts for the ECR, hence, we will focus on the TM/defective BN (TM = Ti ~ Co, Mo, Ru, Rh, and Pt) systems in the following discussions.

2.2. Screening TM/defective BN Nanosheets as ECR Electrocatalysts

To investigate the process of ECR to CH_4 on TM/defective BN, we consider different reaction pathways in this work, as depicted in Figure 1a, that have been proposed as possible reaction pathways for ECR to CH_4 in previous investigations.^[18,21,23,27] By calculating the free energies of adsorbed intermediates along the reaction pathways, we obtain the free energy diagram and the onset potential, U_{onset} , for ECR to CH_4 on various TM/defective BN, as shown in Figure 1b. The onset potentials on Fe/defective BN, Co/defective BN, and Pt/defective BN are -0.52 , -0.68 , and -0.60 V, respectively, which are less negative than those on Cu (100) (-0.78 V),^[23] Cu (211) (-0.67 V),^[23,25] and Cu- C_3N_4 complex (-0.75 V).^[27] We also note that these values are comparable to those on other electrocatalysts with single transition atom or transition metal dimers for ECR to CH_4 , such as Pt@dv-Gr (-0.52 V),^[35] cobalt-porphyrin nanotubes (-0.58 V),^[36] transition metal dimers supported on graphene ($-0.61 \sim -0.70$ V),^[37] and Cu-terminated armchair graphene nanoribbons ($-0.44 \sim -0.58$ V).^[38] These results suggest that the Fe, Co, and Pt TM/defective BN nanosheet systems are excellent potential electrocatalyst materials for ECR to CH_4 . It is noteworthy that Fe and Co are nonprecious metals, therefore, Fe/defective BN and Co/defective BN appear to offer the most cost-effective electrocatalysts for ECR to CH_4 .

2.3. The Electrocatalytic Mechanism of ECR on Fe/defective BN, Co/defective BN, and Pt/defective BN Nanosheets

In order to study the electrocatalytic mechanism of ECR on Fe/defective BN, Co/defective BN, and Pt/defective BN, we calculate the free energy diagrams of ECR to CH_4 through different reduction pathways. Figure 2b–d show the free energy diagrams of ECR to CH_4 on Fe/defective BN, Co/defective BN, and

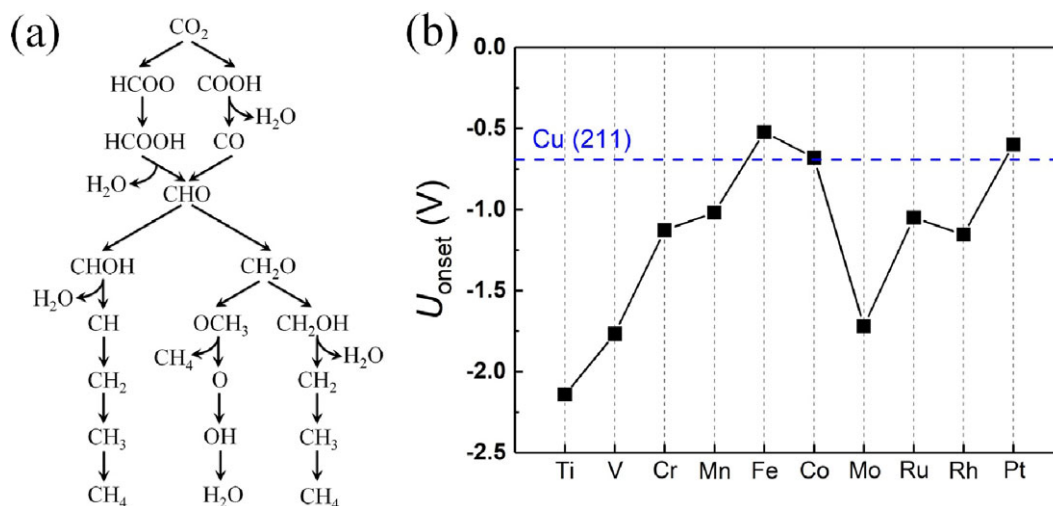


Figure 1. a) Different possible reaction pathways for ECR to CH₄ according to previous investigations. b) The onset potentials for ECR to CH₄ on various TM/defective BN nanosheets. The blue dashed line denotes the onset potential for ECR to CH₄ on Cu (211) surface.

Pt/defective BN, respectively. Clearly, the minimum energy pathways for ECR to CH₄ on those nanosheets are the same, following CO₂ → *COOH → *CO → *CH₂O → *OCH₃ → *O → *OH → H₂O (the corresponding adsorbed intermediate configurations on Fe/defective BN are shown in Figure 2a, which are consistent with those on the (111), (100), and (211) facets of Cu crystal.^[23,25] The adsorbed intermediate configurations on Co/defective BN and Pt/defective BN are similar to those on Fe/defective BN (data not shown here). On Fe/defective BN, the rate-limiting step is the proton/electron-transfer step of *OH (i.e., *OH → H₂O), with an energy barrier of 0.52 eV, while the rate-limiting steps on Co/defective BN and Pt/defective BN lie in the protonation step of *CO (i.e., *CO → *CHO), with energy barriers of 0.68 and 0.60 eV, respectively. The results are also similar to those on the (111), (100), and (211) facets of Cu crystal that the rate-limiting step of ECR to CH₄ is either *OH → H₂O or *CO → *CHO reaction.^[23,25]

2.4. The Origin of High ECR Activity on Fe/defective BN, Co/defective BN, and Pt/defective BN Nanosheets

Insights into the origin of high ECR activity on TM/defective BN nanosheets can guide the design of better electrocatalysts. In Nørskov's method, the limiting potential for each electrochemical step, U_L , at which the electrochemical step of a reaction becomes exergonic (or downhill in free energy), is determined by the free energies of adsorbed intermediates.^[19] In other words, the diverse ECR performance stems from different binding strengths of the adsorbed intermediates on different electrocatalysts. Therefore, it is crucial to identify the relationship between the free energies of adsorbed intermediates and electrocatalytic activity for rational search of more-effective electrocatalysts. Previous works^[23,25] have found that there are seven adsorbed intermediates along the minimum energy pathway for ECR to CH₄ on the (111), (100), and (211) facets of Cu crystal. The first half of the intermediates, that is, *COOH, *CO, *CHO, and *CH₂O, interact with the electrocatalyst surface through a C atom, and

the second half, that is, *OCH₃, *O, and *OH, interact through an O atom. The U_L for each elementary step can be estimated as a function of the electrocatalysts' C or O affinity. Given that the minimum energy pathways for ECR to CH₄ on TM/defective BN are the same as those on Cu crystal, we can correlate ECR activity on TM/defective BN as a function of the electrocatalysts' affinity for C and O. Here we use the free energies of *COOH and *OH to represent the electrocatalysts' affinities for C and O, respectively.

Figure 3 shows the U_L for the two possible rate-limiting steps, that is, *OH → H₂O and *CO → *CHO reactions, on TM/defective BN as a function of the free energies of *OH and *COOH, respectively. The results show that the binding strengths both of *OH and *COOH on TM/defective BN decrease as we move along the row of periodic table of elements, indicating that the TM/defective BN which binds carbon also strongly binds oxygen strongly. Moreover, the U_L for *OH → H₂O reaction becomes less negative as the electrocatalysts' affinity for O (*OH) decrease. On the contrary, with the decrease of the electrocatalysts' affinity for C (*COOH), the U_L for *CO → *CHO reaction become more negative. By comparing the U_L for *OH → H₂O and *CO → *CHO, we find that the U_L for *CO → *CHO reaction is much less negative; it is only for electrocatalysts that have low affinities for both O (*OH) and C (*COOH), such as Co/defective BN and Rh/defective BN, the limitations set by the *CO → *CHO reaction becomes comparable or exceeded to the potential of clearing *OH from the surface. This does indicate that for most TM/defective BN, *OH → H₂O reaction is the rate-limiting step, and *OH removal will likely limit the electrocatalysts' effectiveness due to the strong *OH binding (more negative $\Delta G(*OH)$), however, for TM/defective BN with their low C and O affinity, the rate-limiting step will be set by the CO* → CHO* reaction. Thus, high ECR activity TM/defective BN should have the optimal (moderate) values of electrocatalysts' C and O affinity. As shown in Figure 3, Fe/defective BN, Co/defective BN, and Pt/defective BN nanosheets have moderate affinities for C and O, that is the reason why those electrocatalysts have high activity for ECR to CH₄.

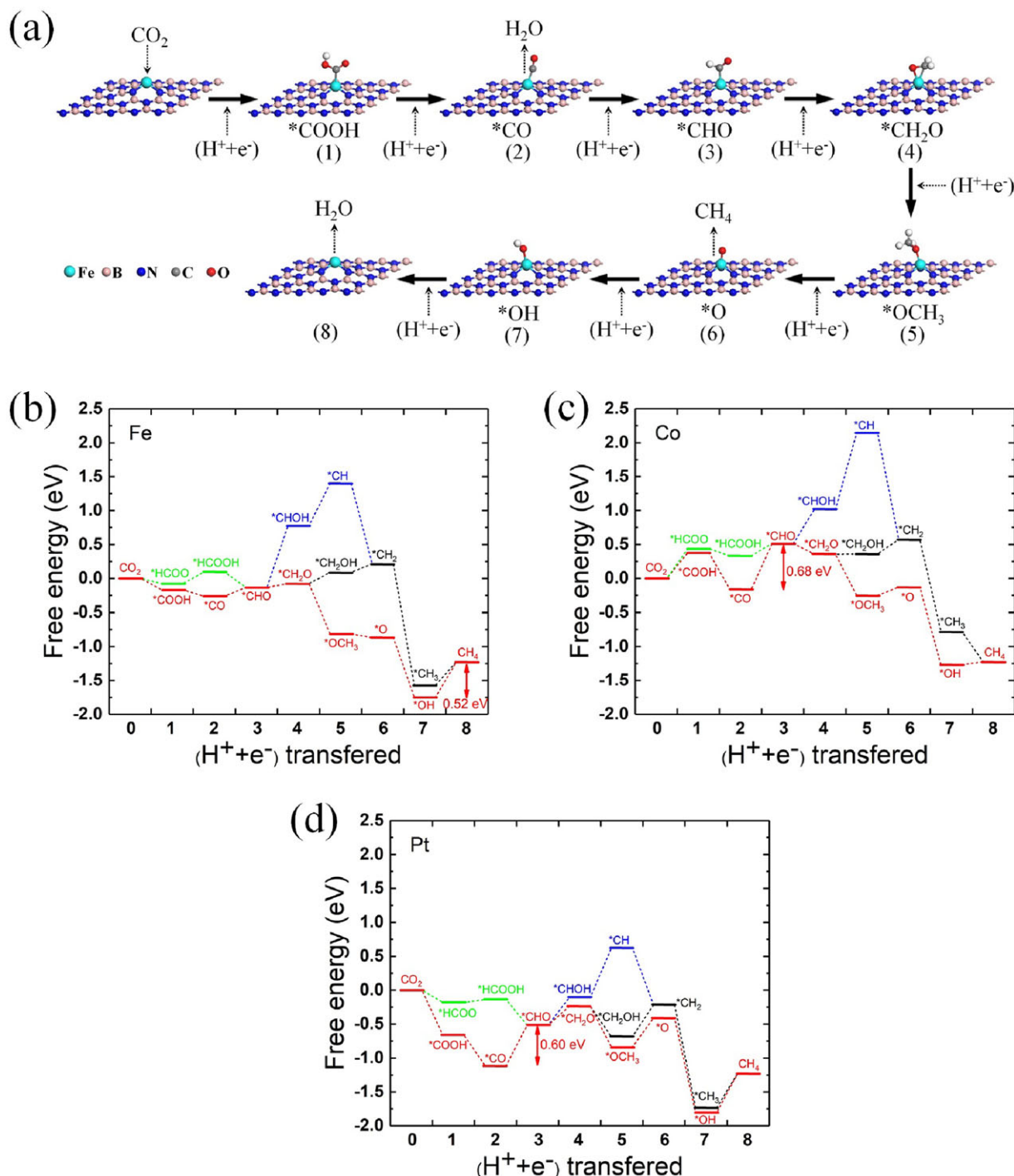


Figure 2. a) The adsorbed intermediate configurations along the minimum energy pathway for ECR to CH₄ on Fe/defective BN nanosheet. The free energy diagrams of ECR to CH₄ on b) Fe/defective BN, c) Co/defective BN, and d) Pt/defective BN. The red arrows denote the rate-limiting steps.

2.5. The Selectivity of ECR to CH₄ on Fe/defective BN, Co/defective BN, and Pt/defective BN Nanosheets

Selectivity is an important parameter for highly efficient electrocatalysts. Because of the complexity of ECR, the electrocatalysts can reduce CO₂ to several products, including the two-

electron products CO and HCOOH, the six-electron product CH₃OH, and the complete eight-electron product CH₄.^[11–14] In addition, HER can be a dominant side reaction that is competitive with the ECR path.^[12,18,25] An effective ECR electrocatalyst should thus show poor activity for the competitive HER.

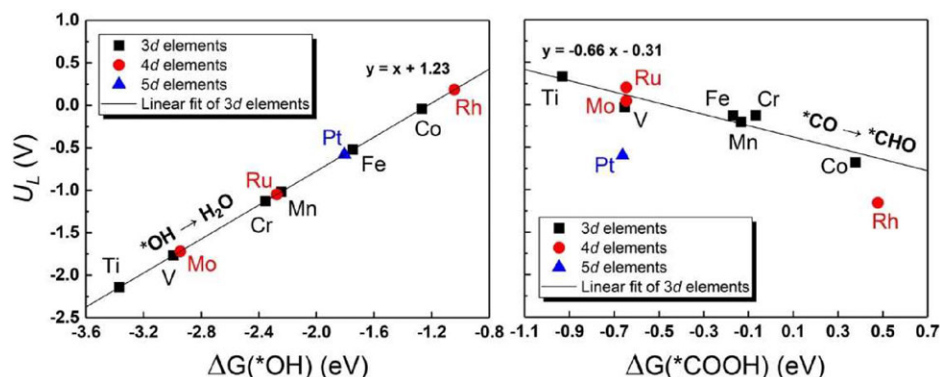


Figure 3. The U_L for two possible rate-limiting steps, that is, $^*\text{OH} \rightarrow \text{H}_2\text{O}$ (left) and $^*\text{CO} \rightarrow ^*\text{CHO}$ (right) reactions, on TM/defective BN nanosheets as a function of the free energies of $^*\text{OH}$ and $^*\text{COOH}$, respectively.

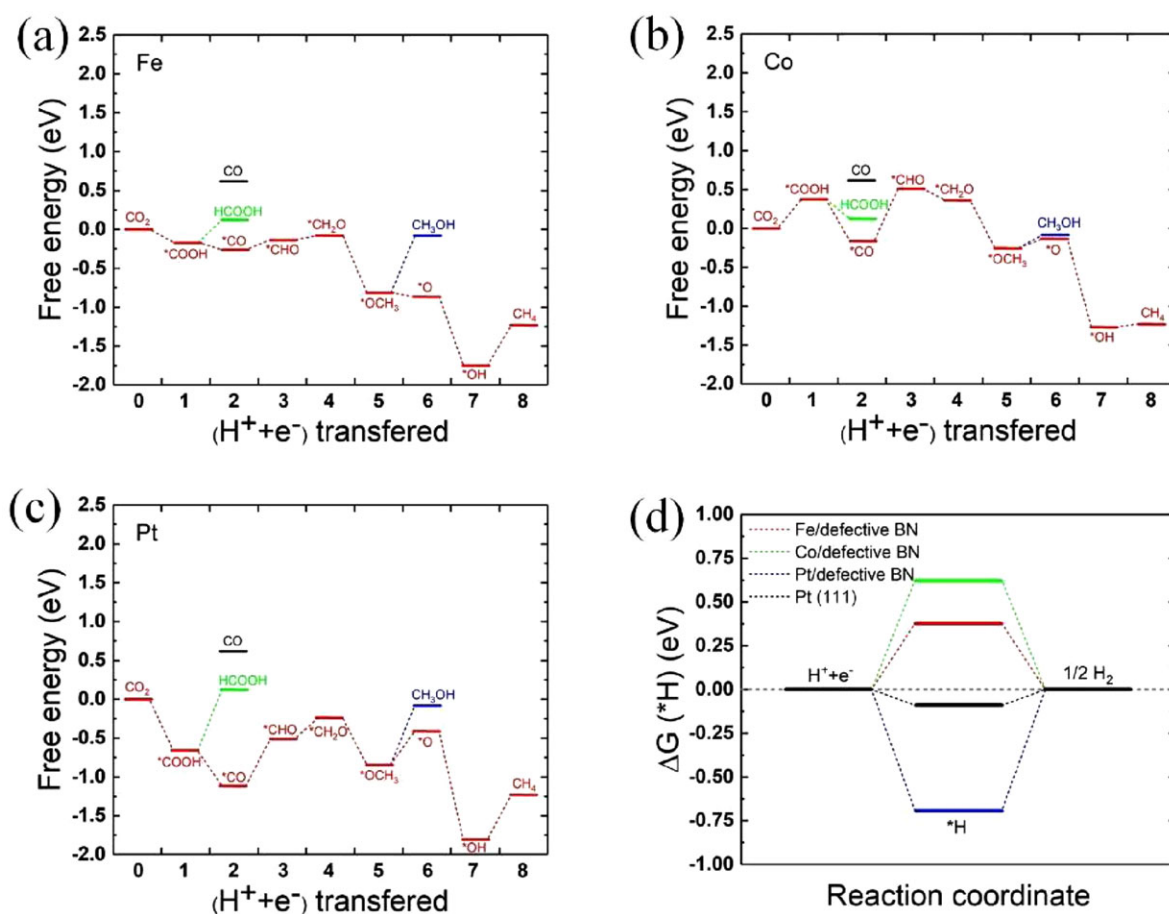


Figure 4. The free energy diagrams of ECR toward the production of HCOOH, CO, and CH₃OH in comparison with that for CO₂ methanation on a) Fe/defective BN, b) Co/defective BN, and c) Pt/defective BN nanosheets, respectively. Here, only the minimum energy pathway is shown. d) The free energy diagram of HER for Fe/defective BN, Co/defective BN, and Pt/defective BN nanosheets. The free energy diagram of HER for Pt (111) is also shown for comparison.

In order to investigate the selectivity of ECR to CH₄ on Fe/defective BN, Co/defective BN, and Pt/defective BN nanosheets, the minimum energy pathways toward the production of HCOOH, CO, and CH₃OH are examined in comparison with the minimum energy pathway for CO₂ methanation on those nanosheets, as shown in **Figure 4a–c**. In general, the

reaction pathways and the free energy diagrams of ECR toward HCOOH, CO, CH₃OH, and CH₄ on Fe/defective BN (**Figure 4a**) and Pt/defective BN (**Figure 4c**) display similar trends, hence here we use Fe/defective BN as an example to explain the selectivity of ECR to CH₄ on those two nanosheets. On Fe/defective BN (**Figure 4a**), the dissociation of $^*\text{COOH}$ to form $^*\text{CO}$ is

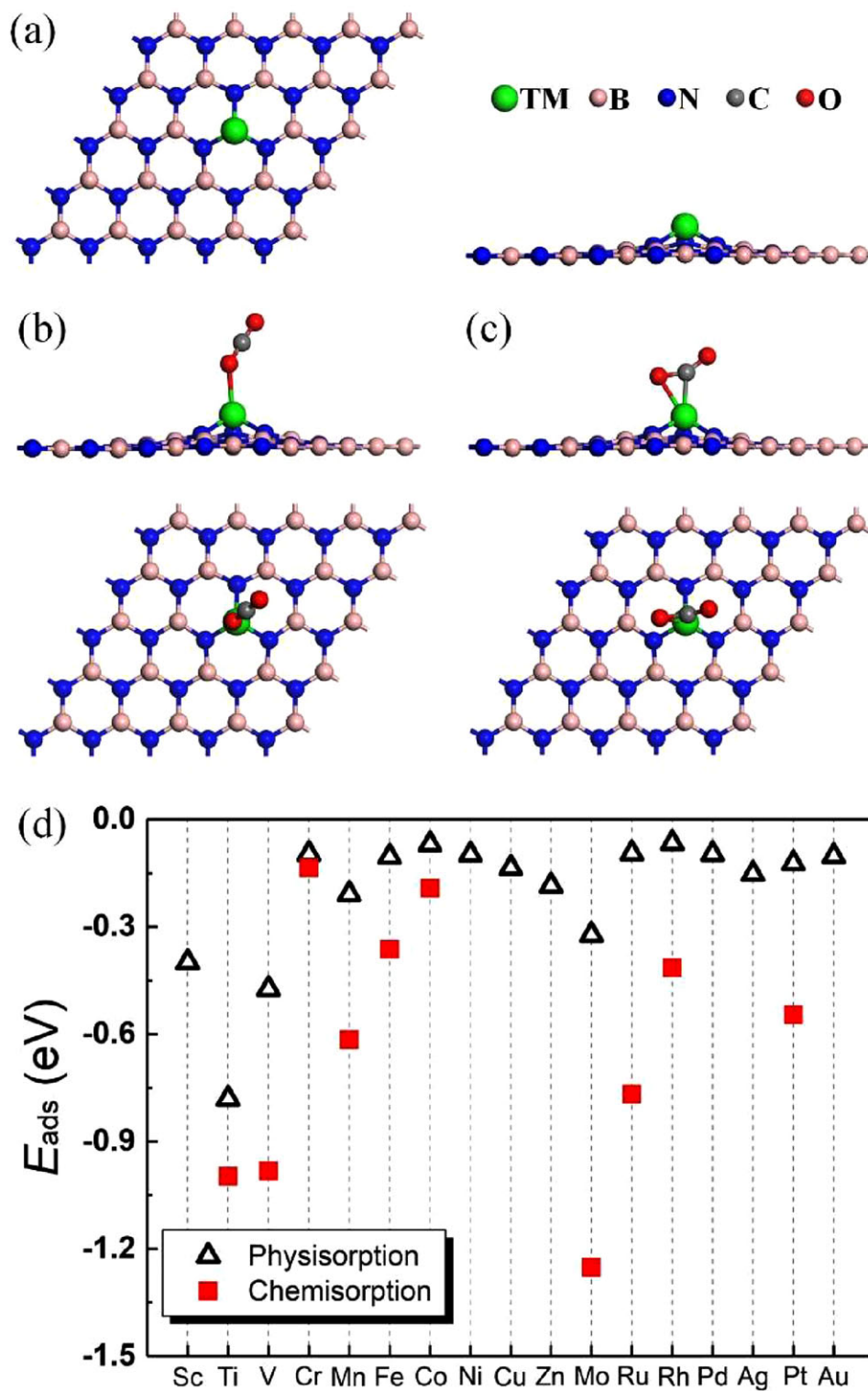


Figure 5. a) Top (left) and side (right) views of a TM/defective BN (TM = Sc ~ Zn, Mo, Rh, Ru, Pd, Ag, Pt, and Au) nanosheet. Optimized structures of CO₂ b) physisorption and c) chemisorption on TM/defective BN. d) The E_{ads} of a CO₂ on various TM/defective BN.

Table 1. Contribution to the free energies of adsorbed intermediates and non-adsorbed gas-phase molecules from ZPE correction, enthalpic temperature correction, and entropy contribution. All are given in eV.

Species	ZPE	$\int C_p dT$	$-TS$
*COOH	0.62	0.10	−0.18
*HCOO	0.62	0.10	−0.23
*CO	0.19	0.07	−0.15
*CHO	0.44	0.09	−0.18
*CH ₂ O	0.76	0.09	−0.19
*OCH ₃	1.11	0.09	−0.18
*O	0.07	0.03	−0.04
*OH	0.36	0.05	−0.08
*H	0.16	0.01	−0.01
CO ₂	0.31	0.10	−0.65
CO	0.14	0.09	−0.67
H ₂	0.27	0.09	−0.42
H ₂ O	0.58	0.10	−0.65
HCOOH	0.90	0.11	−1.02
CH ₃ OH	1.35	0.11	−0.79
CH ₄	1.20	0.10	−0.60

exothermic during the formation of CH₄ (red line), while the hydrogenation of *COOH to give HCOOH possesses a barrier of 0.29 eV (green line), suggesting that the formation of HCOOH is unfavorable for the ECR on Fe/defective BN. The desorption of CO possesses a large barrier of 0.88 eV (black line), which is much higher than that of the hydrogenation of *CO to *CHO (0.13 eV) during the formation of CH₄ (red line), indicating that the formation of CO is also unfavorable for the ECR on Fe/defective BN. The barrier for the hydrogenation of *OCH₃ to form CH₃OH is 0.73 eV (blue line); however, the dissociation of *OCH₃ into *O is exothermic during the formation of CH₄ (red line), which means that the formation of CH₄ is more favorable than CH₃OH production on Fe/defective BN. In a word, all these results show high selectivity of CH₄ on Fe/defective BN and Pt/defective BN nanosheets during the ECR to CH₄. However, the case is different on Co/defective BN (Figure 4b), the free energy of *CHO (red line) is 0.39 eV higher than that of HCOOH (green line), and the barrier for the dissociation of *OCH₃ into *O (red line) is only 0.05 eV lower than that for the hydrogenation of *OCH₃ to form CH₃OH (blue line). These results indicate that the selectivity of CH₄ from HCOOH and CH₃OH on Co/defective BN is not as good as that on Fe/defective BN and Pt/defective BN.

We also calculate the free energy diagram of HER for Fe/defective BN, Co/defective BN, and Pt/defective BN nanosheets, as shown in Figure 4d. The overall HER mechanism can be evaluated with a three-state diagram consisting of an initial H⁺ state, an intermediate *H state, and 1/2 H₂ as the final product.^[39] The $\Delta G(*H)$ is proven to be a key descriptor to characterize the HER activity of electrocatalyst. The optimum value of $|\Delta G(*H)|$ should be zero; for instance, this value for the well-known highly efficient Pt (111) electrocatalyst is near-zero as $|\Delta G(*H)| \approx 0.09$ eV.^[39] Clearly, in terms of the selectivity of H₂ gas production, Fe/defective BN, Co/defective BN, and

Pt/defective BN nanosheets show poor activities for HER with $\Delta G(*H) = 0.38, 0.62,$ and -0.69 eV, respectively, implying that HER is unlikely to interfere as an unwanted competitive pathway to the ECR.

3. Conclusions

In summary, we have carried out a comprehensive study of the potential of single transition metal atoms (Sc to Zn, Mo, Rh, Ru, Pd, Ag, Pt, and Au) supported on the experimentally available defective boron nitride monolayer with a boron monovacancy as an effective electrocatalyst for ECR to CH₄, by means of DFT computations. We found that Fe/defective BN, Co/defective BN, and Pt/defective BN possess outstanding electrocatalytic activities for ECR to CH₄ with quite low onset potentials of $-0.52, -0.68,$ and -0.60 V, respectively, which are less negative than other ECR electrocatalysts, such as Cu (100) (-0.78 V), Cu (211) (-0.67 V), and Cu–C₃N₄ complex (-0.75 V). Given that Fe and Co are nonprecious metals, Fe/defective BN and Co/defective BN are cost-effective electrocatalysts. The high ECR activities of those TM/defective BN stem from the moderate electrocatalysts' affinities for C and O, which modulate the free energies of ECR intermediates in the reaction pathways. Comparing the free energy diagrams of HER and ECR toward HCOOH, CO, CH₃OH, and CH₄ on those TM/defective, we also found that Fe/defective BN and Pt/defective BN show high selectivity of ECR toward CH₄. This finding not only clarifies the ECR mechanism on TM/defective BN nanosheets, but also offers a strategy to design highly active and selective SACs, including nonprecious Fe/defective BN and precious Pt/defective BN, for ECR to CH₄.

4. Experimental Section

All of the spin-polarized DFT calculations were performed using the VASP program,^[40–42] which uses a plane-wave basis set and a projector-augmented wave (PAW) method for the treatment of core electrons.^[43] The Perdew, Burke, and Ernzerhof exchange-correlation functional within a generalized gradient approximation (GGA-PBE)^[44] was used in the calculations, and the van der Waals (vdW) correction proposed by Grimme (DFT-D2)^[45] was employed due to its good description of long-range vdW interactions. For the expansion of wavefunctions over the plane-wave basis set, a converged cutoff was set to 450 eV.

In order to simulate the defective BN monolayer with a boron monovacancy, a 5×5 BN supercell with periodical boundary conditions was used, and then, one B atom was removed to create a boron monovacancy, which provides an anchoring site for a single TM atom (Figure 5a). The vacuum space was set to larger than 18 Å in the z direction to avoid interactions between periodic images. In geometry optimizations, all the atomic coordinates were fully relaxed up to the residual atomic forces smaller than 0.005 eV Å^{−1}, and the total energy was converged to 10^{-5} eV. The Brillouin zone integration was performed on the $(4 \times 4 \times 1)$ Monkhorst–Pack k-point mesh.^[46]

Eight net coupled proton and electron transfer steps are involved in ECR to CH₄ process ($\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$). Each ECR step involves the transfer of a proton coupled with an electron from solution to an adsorbed intermediate on the surface of electrocatalysts. The free energies of the adsorbed intermediates in reaction pathways were calculated based on a computational hydrogen electrode (CHE) model proposed by Nørskov et al.^[21,23] In this model, the free energy changes at each electrochemical step involving an proton-electron transfer are calculated using the definition that the free energy of ($\text{H}^+ + \text{e}^-$) equals to $\frac{1}{2}\text{H}_2(\text{g})$ for

standard hydrogen electrode (SHE). According to this method, the free energy change of the reaction, ΔG , was calculated as the difference between the free energies of initial and final states as^[21,23]

$$\Delta G = \Delta E + \Delta ZPE + \Delta \int C_p dT - T \Delta S \quad (1)$$

where ΔE corresponds to the total energy change directly obtained from DFT calculations, ZPE is the zero-point energy, C_p is the heat capacity, T is temperature, and S is the entropy. Here, zero-point energies, heat capacities, and entropies of adsorbed intermediates and non-adsorbed gas-phase molecules were adopted from the previous literature, as listed in Table 1.^[21,23] The adsorbate solvation effects were included approximately in the same manner as in the previous studies: adsorbates *OH, *R-OH, *CHO, and *CO are stabilized by -0.5 , -0.25 , -0.1 , and -0.1 eV, respectively.^[21,23]

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

CO₂ methanation, defective boron nitride monolayer, electrochemical mechanisms, first principle calculations, single-atom electrocatalysts

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